Wet and dry deposition of atmospheric nitrogen in three hydrographic basins in Cuba

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Abstract Acid deposition remains an important environmental issue in Europe and North America. Furthermore, it is emerging in new geographical areas, including parts of South/Central America. In these areas, emissions of nitrogen oxides are increasing rapidly as industrialization proceeds and the use of fossil fuels increases. In Cuba, main atmospheric nitrogen deposition compounds varies approximately from 19.3 to 71.2 kg-N ha^{-1} $year^{-1}$ in rural areas. The oxidized nitrogen forms being provided 34% as average and wet deposition depends on the Cuba tropical rain climate features. The NH_3 and ammonium are the most important elements in Cuban tropical conditions. This paper is showing more relevant results about main compounds of atmospheric nitrogen in Cuba and its potential impact on environment.

Key words acid deposition; nitrogen compounds; wet deposition; oxidized nitrogen

INTRODUCTION

Human efforts to produce food and energy are changing the nitrogen (N) cycle of the Earth. Many of these changes are highly beneficial for humans, while others are detrimental to people and the environment. These changes transcend scientific disciplines, geographical boundaries, and political structures. They challenge the creative minds of natural and social scientists, economists, engineers, business leaders, and decision makers (Cowling, 2001).

Nowadays, most anthropogenic activities endanger the functioning and structure of natural and semi-natural ecosystems due to the effects on the endemic species of animals and plants. One of the major dangers is the increase of atmospheric pollution by nitrogen compounds during recent decades. The most important messages for environmentalists and policy makers are:

(a) Increase circulation of nitrogen in the atmosphere and biosphere is occurring in all parts of the globe.
(b) Nitrogen has a range of well-understood beneficial and detrimental consequences for humans and environment.
(c) Scientists and decision makers needs to work together to develop integrated approaches to solve nitrogen related problems.

Knowledge of the atmospheric component of the nitrogen cycle is of great importance because of the different compounds involved, their chemistry and the atmospheric pollution they cause. These pollutants have the capacity to affect human health, different aquatic and terrestrial ecosystems, and climate.

In many areas, soil acidification due to nitrification of ammonium deposited from the atmosphere is comparable to that from the deposition of nitric acid (Rodhe, 1995). Currently ammonia (NH_3) emissions are of the same magnitude as that of nitrogen oxides (NO_x) and sulphur dioxide (SO_2) emissions and are potentially even more acidifying.

The nitrogen compounds are nitrogen oxides (nitrogen dioxide and nitric oxide), ammonia (NH_3), nitrate (NO^-_3) and ammonium (NH^+_4) in aerosols and rainfall. In this paper, the deposition of atmospheric nitrogen compounds at three hydrographic basins in Cuba, is discussed for the period 1985 to 2005. The most relevant results regarding the main compounds of atmospheric nitrogen in Cuba and its potential impact on environment, are presented.

MATERIALS AND METHODS

In preparing this paper, data from the air pollution control station network of the Meteorological Institute of the Cuban Ministry of Science, Technology and Environment were used (Fig. 1). The

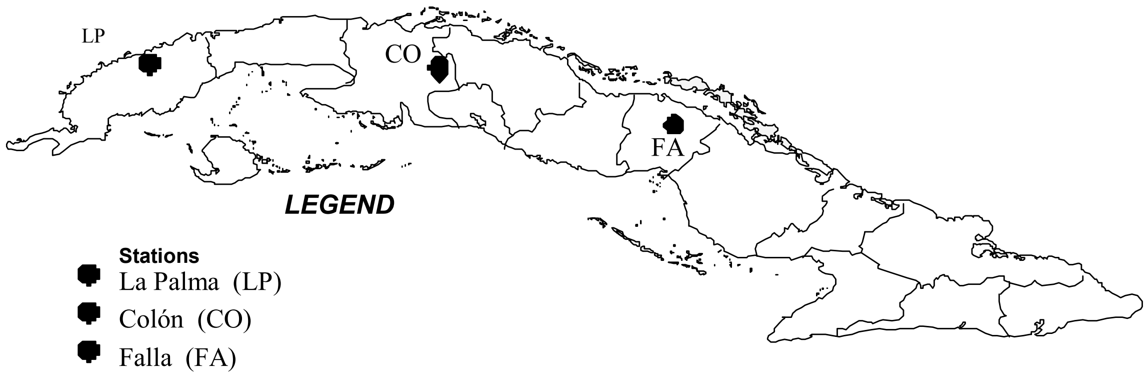

Fig. 1 Monitoring stations for nitrogen compounds.

work of this network is conducted using methodologies recommended by the World Meteorological Organization for monitoring and chemically analysis of the above-mentioned compounds at the regional level. The stations are situated in three important hydrographic basins.

For calculation of wet and dry deposition of atmospheric nitrogen, the concentrations expressed in μg m^{-3} for NO_2, NO, NH_3, NO_3^- and NH_4^+ were converted into nitrogen (N). Concentrations in rainfall are expressed as mg L^{-1}. Samples were collected and analysed using World Meteorological Organization approved methods for rainfall, aerosols and gases; all methods were quantitatively determined colorimetrically. Nitrates react in the acidified sample with 2,4 xylenol, which is then extracted with synthetic toluene and finally re-extracted from the synthetic toluene with sodium hydroxide solution. Ammonium ion concentration is reacted with hypochlorous acid, phenol and a manganese sulphate solution. The blue indophenol formed is quantitatively determined colorimetrically. Ammonia (NH_3) in air is collected by passing it through dilute sulphuric acid and determined using a minor modification of the indophenol technique (WMO, 2004).

For the dry deposition flux, because of the known deficiencies of existing monitoring methods, the quantities were recalculated using the deposition velocity (Cuesta *et al.*, 1998) and the concentrations obtained from monitoring. For wet deposition fluxes, the mean heavy concentrations for each year (starting from a summary of monthly samples) and the rainfall quantities were used for both concentrations. Deposition fluxes are expressed in kg-N ha^{-1} $year^{-1}$. The values of deposition velocity were obtained after analysis of data reported by different authors and selection of those which are most adapted to the climatic conditions of Cuba (Whelpdale & Kaisser, 1995; Cuesta *et al.*, 2001); they are shown in Table 1.

All statistical analyses were performed in SPSS Plus. In addition, trends in the concentration data 1985–2005 were analysed. This allows the behaviour of both the natural and anthropogenic sources of the above-mentioned compounds to be understood.

Table 1 Selected values of the deposition velocity in cm s^{-1} for the gases and aerosols in dependency of land use and climatic conditions.

Stations	NO_2	NO	NH_3	NO_3^-	NH_4^+
La Palma	0.2	0.15	0.5	0.5	0.5
Colon	0.2	0.15	0.3	0.2	0.2
Falla	0.2	0.15	0.3	0.2	0.2

RESULTS AND DISCUSSION

The total deposition values (dry and wet) for the main nitrogen compounds at the three stations are shown in Fig. 2. La Palma's station presents the highest deposition values for ammonia indicating a bigger deposition velocity for this compound. Colon's station presents the highest values of ammonium in the rainfall. The strength of the sources of N compounds, and the high rainfall at these stations are due to its geographical location in the middle of the country, and in addition it is a farming and livestock zone. Farming is recognized as major source of atmospheric ammonia (NH_3) in Europe and contributes about half of the global NH_3 emissions (Sommer & Hutchings, 1995).

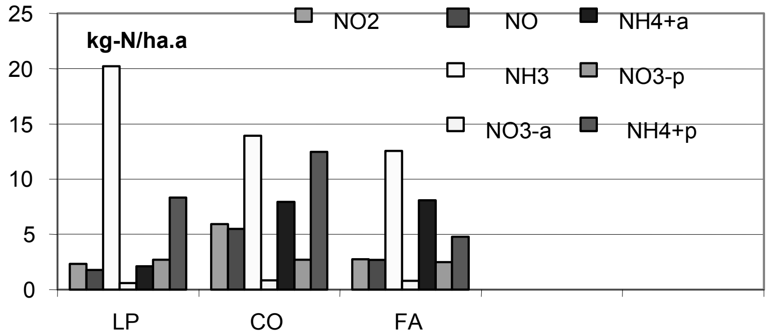

Fig. 2 Annual mean of nitrogen deposition by compound and station (1985–2005). LP is La Palma; Co is Colon; FA is Falla; p is precipitation, a is aerosol.

In general these annual values are similar to those reported in most of Europe and North America (Driscoll, 2001), except in the large urban and industrialized centres, where the deposition in Europe is significantly higher. The annual values at the three stations vary from a minimum of 19.3 kg-N ha^{-1} $year^{-1}$ recorded at Falla station in 1998, where it is due to the low values of NH_3, to a maximum of 71.2 kg-N ha^{-1} $year^{-1}$ in 2001 at La Palma station, where the ammonia deposition was considerably higher. As can be appreciated, in the tropical Cuban conditions, the natural and anthropogenic emissions of ammonia are very important in the biogeochemical cycle of nitrogen.

Wet deposition of inorganic nitrogen from nitrate in the USA during 2000 varied from 1 to 20 kg-N ha^{-1} $year^{-1}$ or more. On the other hand, wet deposition of ammonium ranged from 1 to 4.5 kg-N ha^{-1} $year^{-1}$. The wet deposition of nitrate in Cuba is similar to that in the south of the USA, but wet deposition of ammonium is moderately higher in Cuba than in the USA (NADP, 2001).

In Cuba, the data from these stations show that wet deposition of nitrogen represents more than 20% of the total deposition. Although as a general rule the dry deposition is greater, at Colon and La Palma stations, where rainfall is high, wet deposition has even greater influence.

The values obtained for Cuba refer to the main kinds of oxidized nitrogen species; they represent 34% on average. However, Colon and La Palma stations receive the lowest amount of oxidized nitrogen because of the great importance of natural reduced nitrogen sources. Ammonia (NH_3) and ammonium are the most important nitrogen species in the tropical conditions in Cuba.

These values reflect a very large amount of ammonia deposition, so it is considered that over short timescales the ammonia neutralizes the atmosphere's acidity and associated damage. On the another hand, it can produce soil and underground waters acidification over longer time periods.

Responses of terrestrial ecosystems to anthropogenic nitrogen inputs are likely to vary geographically. However, not all ecosystems respond to N deposition similarly; their response depends on factors such the successional state, ecosystem type, N demand or retention capacity, land-use history, soils, topography, climate, and the rate, timing, and type of nitrogen deposition (Matson *et al.*, 2002).

La Palma station is representative of the forest ecosystem of western Cuba and at this moment this station receives the 20% from acid deposits. The soil of this region is classified with very high acidity (pH 4.1–4.5), and will be very sensitive to acid deposition; this can produce harmful ecological risks in soil productivity, affecting trees growing in forest areas, as well as the productivity of some other crops. Forest areas are able to receive from five to six times more dry deposition (gas and aerosol) due to the greater deposition flux that they generate, and so make this region ecologically more sensitive. The response and reaction of forest ecosystems to chemical changes in the environment are complex.

Through studies of the behaviour of diverse nitrogen species at the La Palma station, it is possible to see (Fig. 3) that the NH_3 and ammonium (rainfall and aerosol) contributions are greater than 70% of the total nitrogen deposition. These values reflect the very large proportion due to the ammonia deposition, and it is considered that the ammonia neutralizes, in the short term, the atmosphere's acidity, and also it avoids the damages. On the other hand, it can produce soil erosion and underground waters acidification in the longer term (Galloway, 1995).

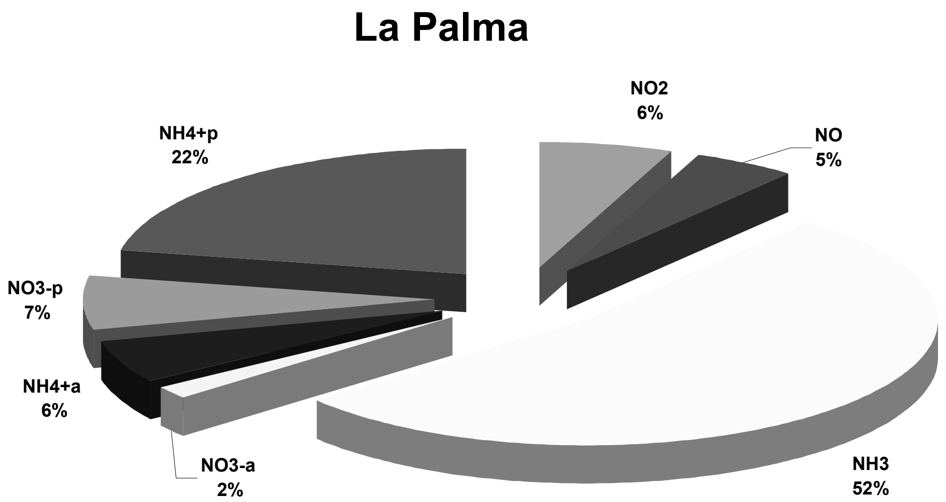

Fig. 3 Breakdown of nitrogen deposition by compound for La Palma station.

Another of the potential effects that can provoke deposition of oxidized nitrogen compounds is acidification of surface freshwater streams and lakes; this causes reduction of the bicarbonate ion and the increase of nitrate concentrations, which produces and increase concentrations of some metals in freshwater bodies. Metals such as aluminium, cadmium, zinc, lead and mercury are very toxic and can be ingested by different types of aquatic life, and through alimentary chains, even arrive in man's food.

Some nitrogen compound concentrations (see Table 2) showed a significant trend in the period from 1985 to 2005.

La Palma, Colon and Falla rural stations present a significant trend for NO_2 and NH_3 concentration increase (Fig. 4). These rural stations seem to be influenced by the biomass burning for

Table 2 Direction of the trend for nitrogen atmospheric compounds.

Stations	NO_2	NO	NH_3	$NO_3^+{}_{(a)}$	$NH_4^+{}_{(a)}$	$NO_3^+{}_{(p)}$	$NH_4^+{}_{(p)}$
La Palma	+	+	+	–	+	–	+
Colón	+	+	+	–	–	–	–
Falla	+	+	+	–	–	–	–

Note: (–) direction to decrease, (+) to increase, (a) aerosol, (p) precipitation.

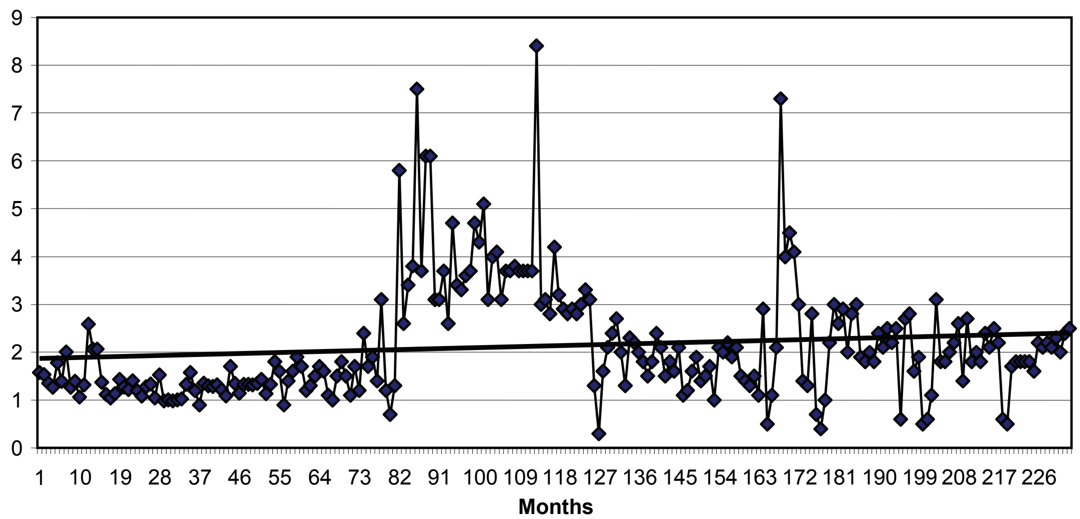

Fig. 4 The NO_2 concentrations trend in Colon station. Units of vertical axis are mg-N m^{-3}.

energy purposes and it is possible that the change in land use and application of fertilizers also influences this increase. In addition, the trend of an increase of ammonium aerosols is very important and its increase has been significant at rural La Palma station, mainly caused by the use of ammonia as a fertilizer in these regions. The increase of ammonium in rainfall is only present at La Palma station.

The potentially harmful effects due to acid deposition influence the aquatic and terrestrial ecosystems, and also cause corrosion of materials and human health problems, so a system of integrated monitoring must be imposed to assess and to be able to mitigate its effects.

CONCLUSIONS

In Cuba, the total deposition for main nitrogen compounds varies from 19.3 to 71.2 kg-N ha^{-1} $year^{-1}$. Dry deposition of nitrogen represents somewhat more than 70% of total nitrogen deposition. NH_3 is very important in dry deposition. The relative weights of dry and wet deposition depend on the characteristics of Cuba's rainy tropical climate. Oxidized forms of nitrogen contribute to approximately 34% of the total.

The Colón and La Palma stations receive the lowest amount of oxidized nitrogen because of greater strength of natural reduced nitrogen sources. NH_3 and ammonium are the most important nitrogen compounds in the tropical conditions in Cuba.

It is necessary to maintain systematic monitoring at the rural La Palma, Colón and Falla stations because trends for increasing concentrations of oxidized nitrogen compounds could potentially cause future damage to the agriculture and forest of these regions.

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